Updated: 17 April 2013

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CEE 577: Surface Water Quality Modeling

Lecture #36

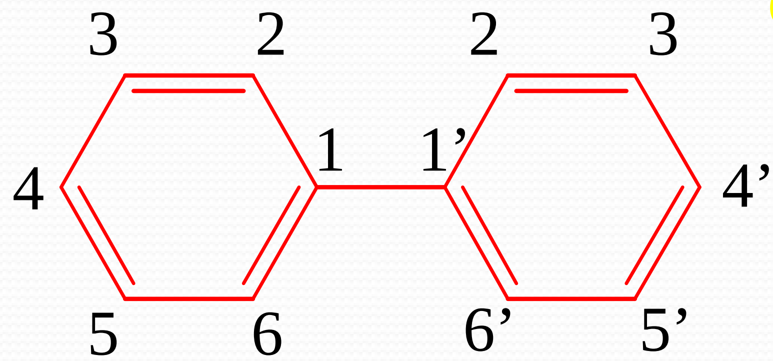
Toxics: PCBs in the Great Lakes

(Jeremiason et al., 1994)

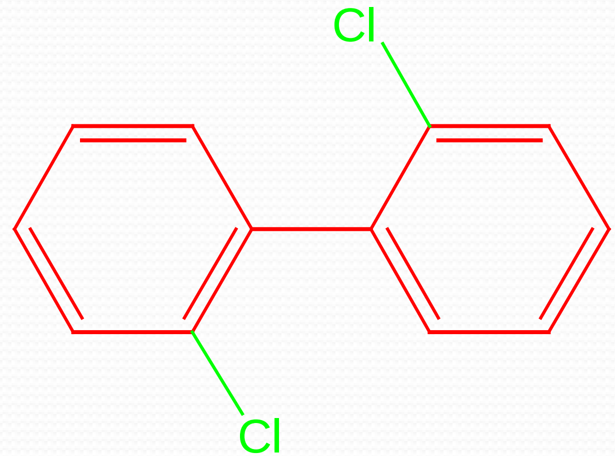
What are the PCBs

Homologs (11)
Isomers (1-46)
Congeners (209)

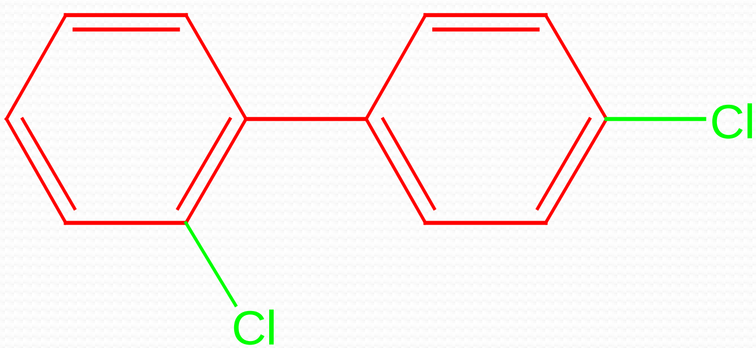
- Biphenyl



- 2,2’ - Dichlorobiphenyl



- 2,3’ - Dichlorobiphenyl



History

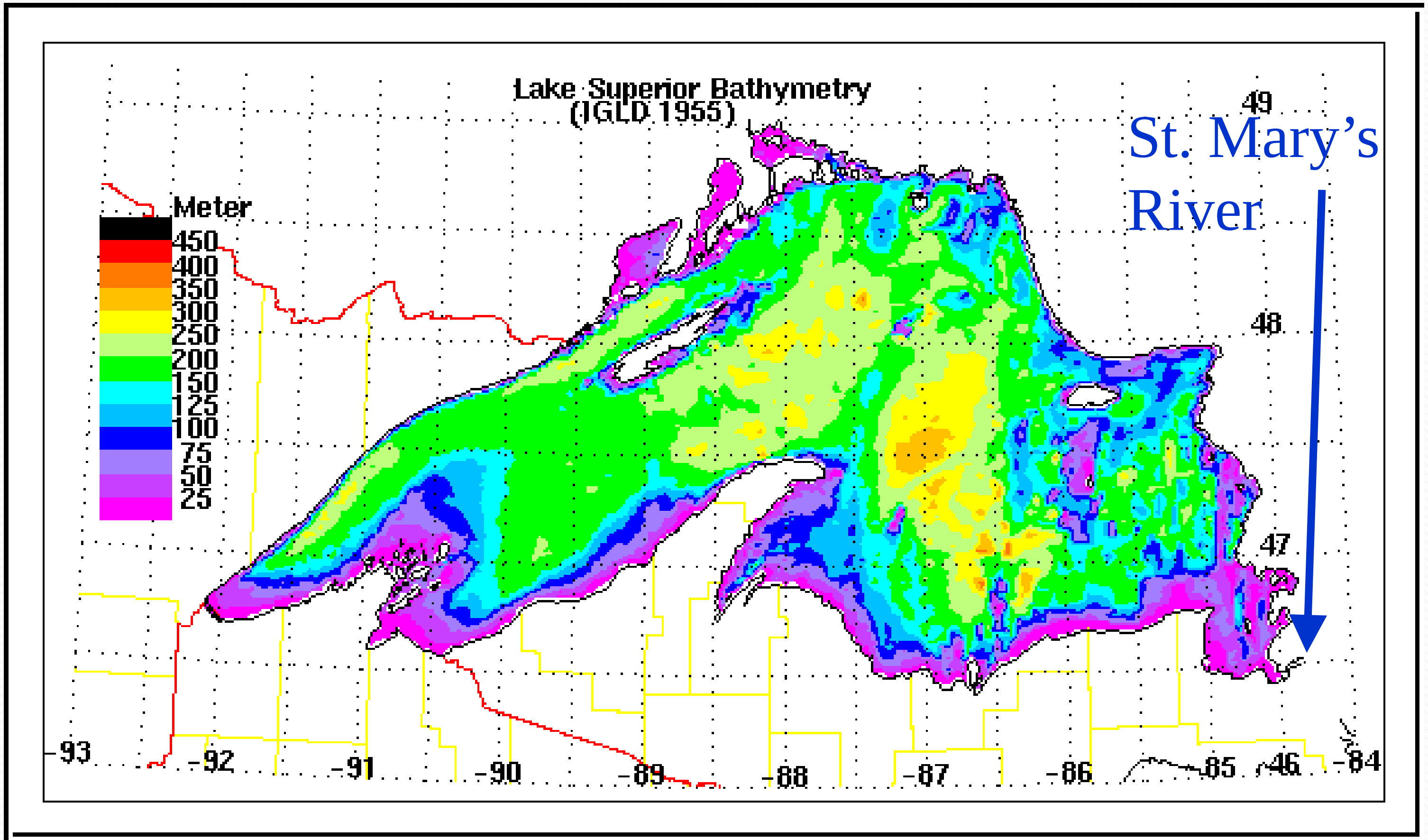
- 1930: Monsanto is major US producer
- 1970: Monsanto decides to sell PCBs only for closed use
- 1975: NY State warns public about salmon and bass in Hudson
- 1979: PCB manufacture banned in US
- 1982: NY State begins dredging “hot spots”
- 1990: all PCB-containing equipment must be removed from US public buildings

Arochlor Mixtures

- Arochlor 12xx (xx=% chlorine)
  - 1221: 50% Cl_1, 35% Cl_2
  - 1232: 26% Cl_1, 29% Cl_2, 24% Cl_3
  - 1242: 13% Cl_2, 45% Cl_3, 31% Cl_4
  - 1248: 49% Cl_4, 27% Cl_5
  - 1254: 15% Cl_4, 53% Cl_5, 26% Cl_6
  - 1260: 12% Cl_5, 42% Cl_6, 38% Cl_7
  - 1262: no data
  - 1268: no data

PCBs in the Lake Superior

- Reference: "PCBs in Lake Superior, 1978-1992: Decrease in Water Concentrations Reflect Loss by Volatilization," by Jeremiason, Hornbuckle and Eisenreich, Environmental Science and Technology, 28:903 (1994)



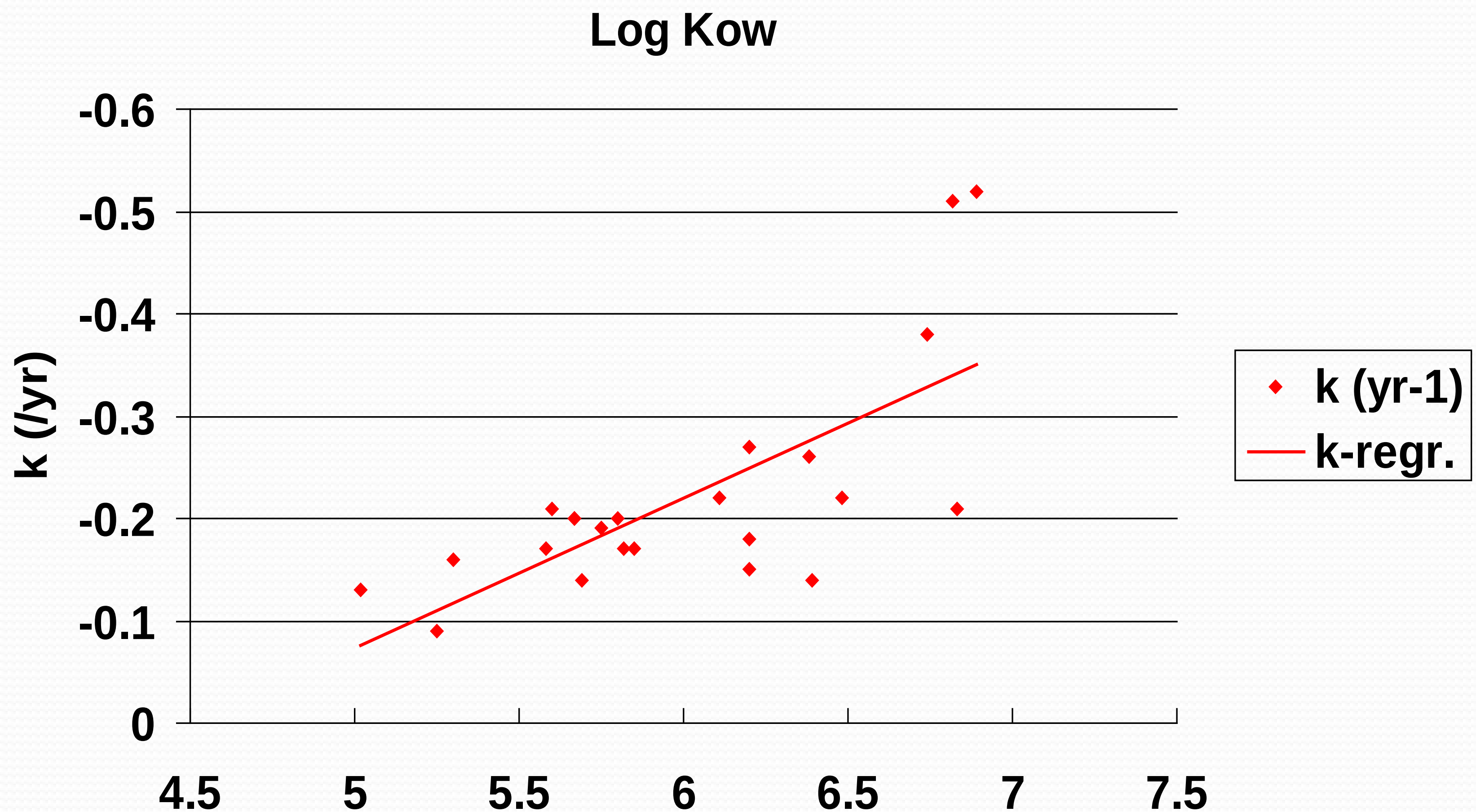
Empirical Models

$$\sum\nolimits_{25} PCB = \left(\sum\nolimits_{25} PCB_o\right) e^{-0.20t}$$

$$\sum\nolimits_{82} PCB = \left(\sum\nolimits_{82} PCB_o\right) e^{-0.22t}$$

- Data tell us that about 26,500 kg has been lost from the water column between 1980 and 1992

Loss rate and K_{ow}'s



Areal Sediment Burden (mass)

- Estimated at 4900 kg in 1986
  - using data from sediment cores
  - relatively small compared to total lost from water column (26,500 kg from '80 to '92)

$$\sum PCB_{areal} = \sum PCB_i (1 - \phi_i) \rho_s z_i$$

PCB conc. (ng/g-dry sediment) in depth increment "i"

Porosity of increment "i"

Thickness of depth increment "i"

Inputs

$$
\begin{aligned}
W &= Qc \\
&= 5.4x10^{13}\, L/yr\left(2ng/L\right) \\
&= 110\, kg/yr
\end{aligned}
$$

- Riverine
  - Known Q
  - Estimate c from analysis of pristine rain
- Other
  - estimates from industrial, municipal, (urban) runoff and storm sewer flows gives a combined total of about 40 kg/yr

Inputs (cont.)

- Direct Atmospheric deposition
  - wet deposition

precipitation

Surface Area

$$F_{wet} = \sum PCB_{T,rain} P(SA)$$
$$= 2ng/L(76cm)8.21x10^{10} m^2$$
$$= 125kg/yr$$

  - dry deposition
    - calculated for 4 seasons, then averaged

Dry particle deposition velocity (0.2 cm/s)

$$F_{dry} = \sum PCB_{T,air} V_d \phi (SA) f_d$$
$$= 32kg/yr$$

Fraction of year when it is not precipitating (0.9)

Fraction of PCBs associated with particles

Outputs

- Outflow
  - St. Mary's River

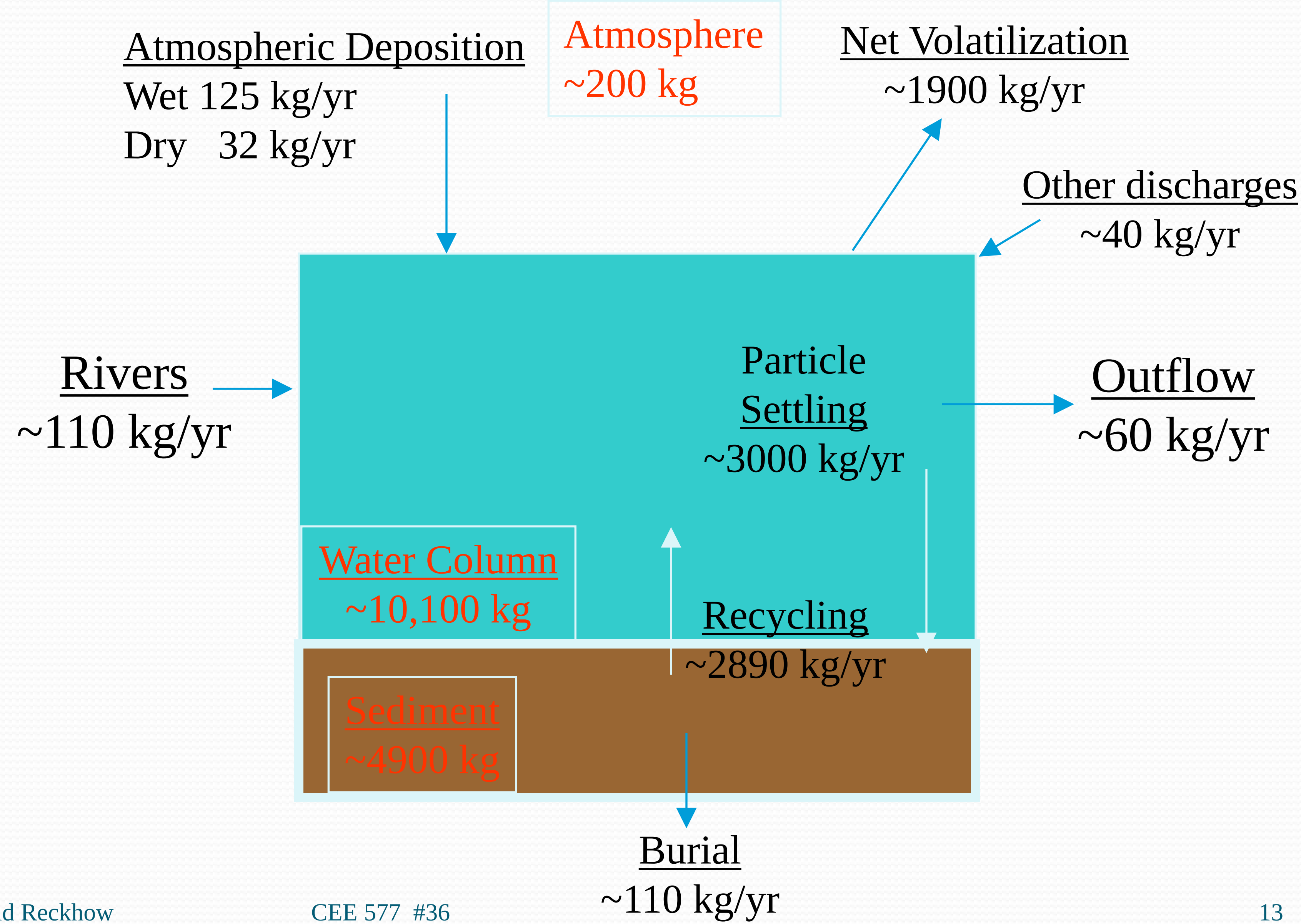
$$W_{outflow} = 7.1x10^{13} L/yr(0.84ng/L) = 60kg/yr$$

- Burial (net loss to sedimentation)
  - estimated at 110 kg/yr from sediment cores collected in 1986 and 1990
- Net Volatilization
  - true volatilization minus gas absorption
  - assumed to account for missing flux

Reactions

- NONE!
  - “evidence does not exist to support PCB degradation in Lake Superior or any other oligotrophic, aerobic system exhibiting low ambient concentrations”

PCB Mass Balance in Lake Superior, 1986



Congener-specific sedimentation

- Calculation of first-order net sedimentation rate

Mass sedimentation rate (mg/cm²/yr)

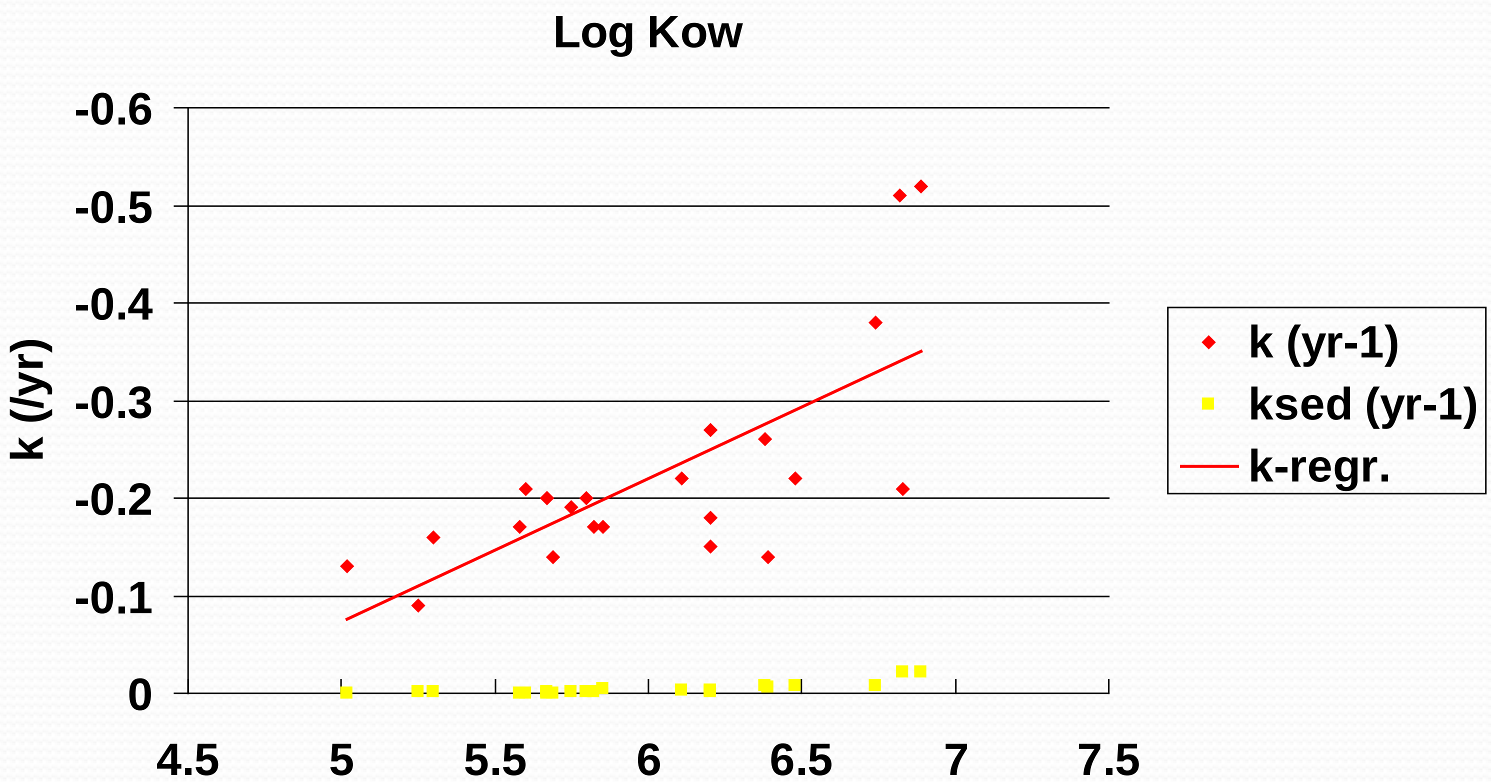
Inventory (or areal TSS)

Fraction particulate

$$k_{sed} = \frac{\left[W_{sed} \big/ INV_{w} \right] f_{p}}{RR}$$

Recycling ratio = downward flux (from sed trap) divided by the accumulation in the sediment

Sedimentation vs overall loss rate



Two Film Volatilization Model

- Jeremiason's equation $$k_{vol} = \frac{K_{ol}}{h} f_w$$
  - Same as Chapra's $$k_v = \frac{v_v}{H_1} f_{d1}$$
- Where:

$$\frac{1}{K_{ol}} = \frac{RT}{k_a H} + \frac{1}{k_w}$$

Estimating 2-film parameters

- The gas film coefficient

$$k_{a,H_2O} = 0.2u_{10} + 0.3$$

$$k_{a,PCB} = k_{a,H_2O}\left(\frac{D_{PCB,air}}{D_{H_2O,air}}\right)^{0.61}$$

- The liquid film coefficient

$$k_{w,CO_2} = 0.45u_{10}^{1.64}$$

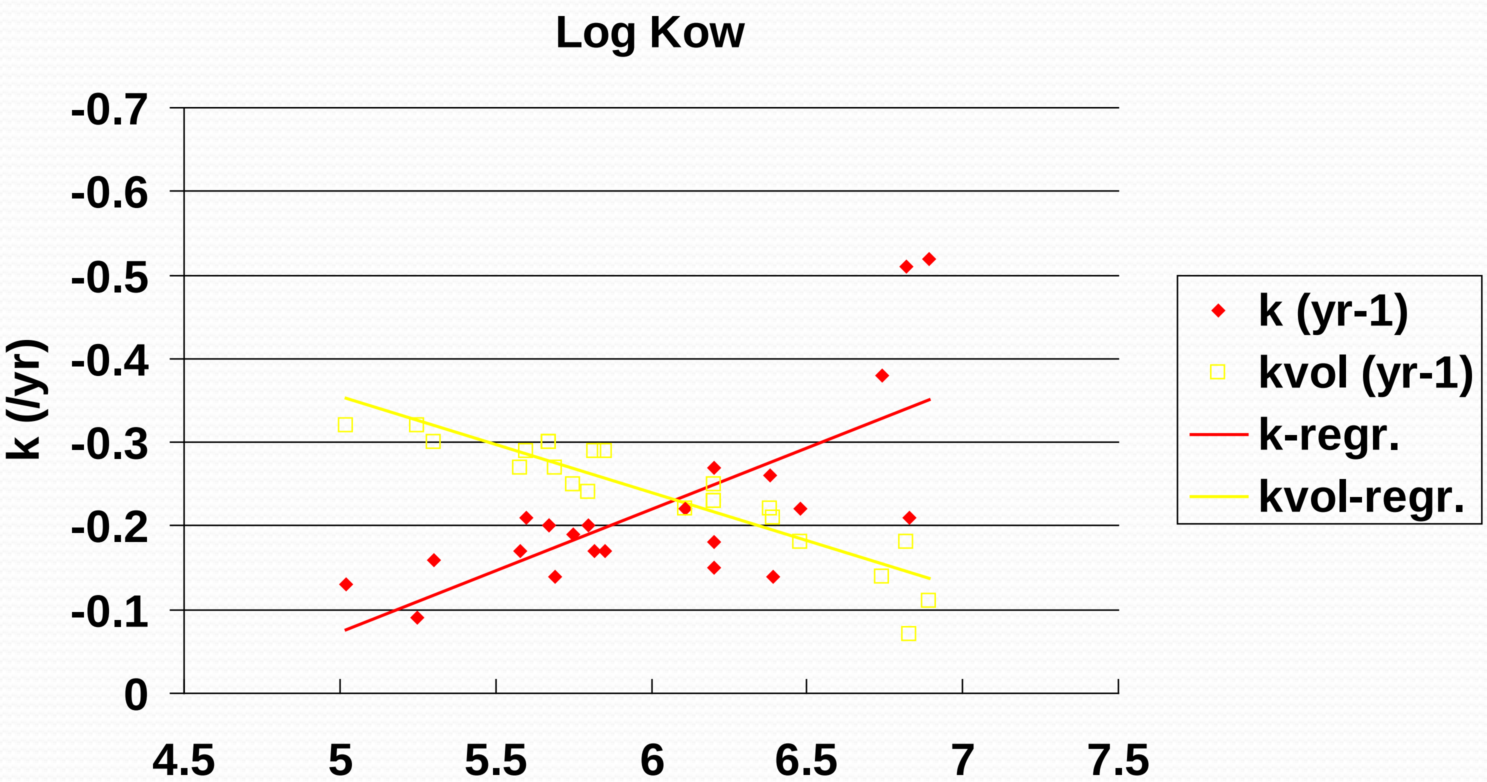
$$k_{w,PCB} = k_{w,CO_2}\left(\frac{Sc_{PCB}}{Sc_{CO_2}}\right)^{-0.5}$$

Kinetic viscosity: molecular diffusivity

$$Sc = \frac{\mu}{\rho . D_V}$$

Schmidt Number

Volatilization vs overall loss rate



- To next lecture